KU LEUVEN

Liquid metal salts: ionic liquid electrolytes for high-rate electrodeposition

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Acknowledgments

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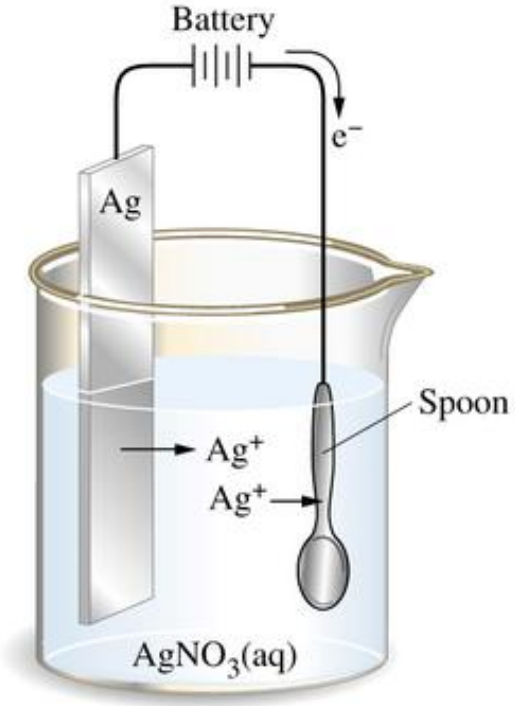
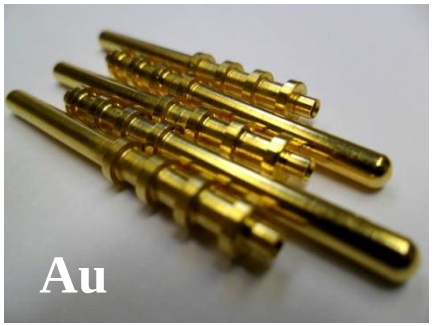
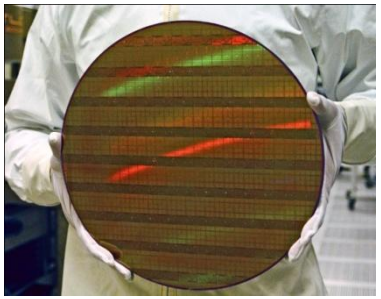
- Dr. Phil Dale (Univ. Luxembourg)

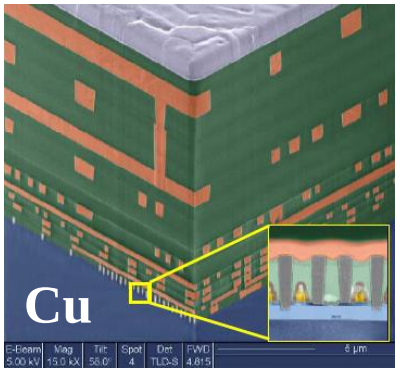
Electrodeposition

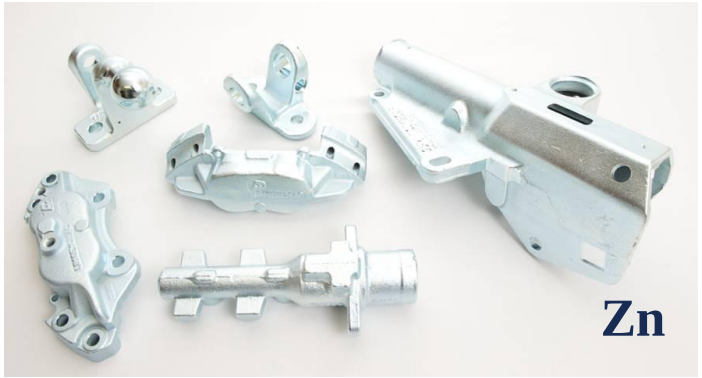
- Corrosion protection
- Decorative coatings
- Layers with electric or electronic properties
- Functional coatings (e.g. low friction)





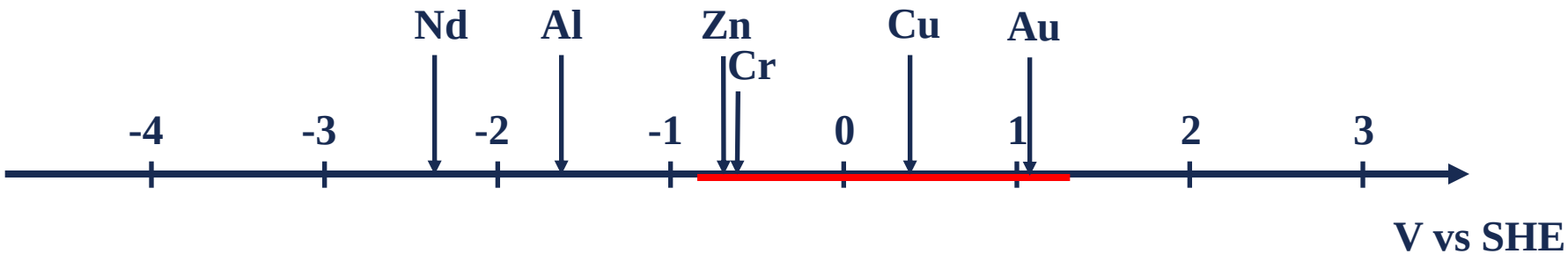






Electrodeposition

- Limited electrochemical window of aqueous solutions



- Passivation of moisture-sensitive substrates

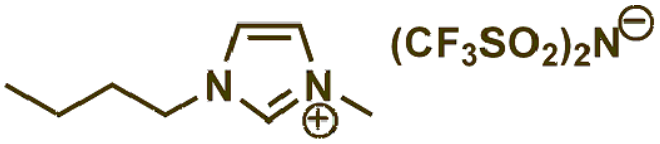
  $Al \rightarrow Al_2O_3$

  $Ti \rightarrow TiO_x$

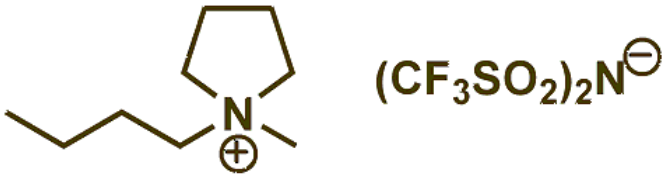
  $Ta \rightarrow Ta_2O_5$

Electrodeposition in ionic liquids

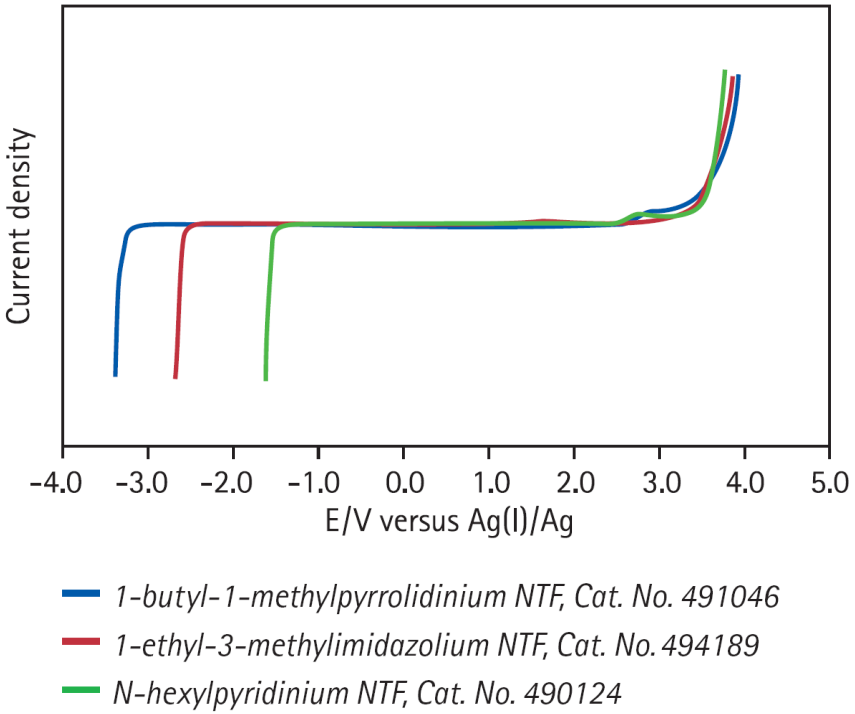
- Wide electrochemical window: up to 5 V (1.23 V in water)
- Can be used at temperatures above 100 °C
- Very low vapor pressure; no evaporation of electrolyte



[BMIM][Tf_2N] or [C_4mim][Tf_2N]



[BMP][Tf_2N] or [C_4mpyr][Tf_2N]

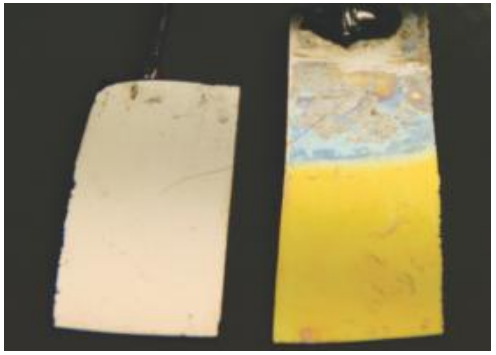


Source: Merck catalogue

Solubility issues

- High concentrations of metal ions are required for electrodeposition
- Solubility of metal salts in ionic liquids with weakly coordinating anions is often low

  - chloride salts are poorly soluble in [BMP][Tf_2N]
  - $M(Tf_2N)_x$ salts have to be used
- Chloride salts are well soluble in dicyanamide ionic liquids, but anodic electropolymerization at inert electrodes



- Chloride salts dissolved in chloride ionic liquids form anionic complexes that are not electroactive, e.g. $[AlCl_4]^-$ or $[CoCl_4]^{2-}$

Concept of liquid metal salts

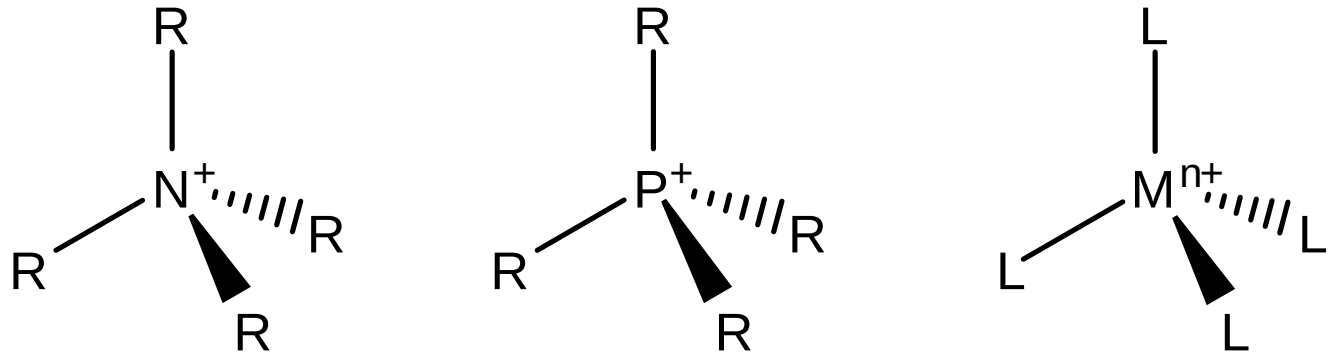
- New approach: make metal part of ionic liquid cation
  - No longer a need to dissolve metal salts
  - High metal concentrations
  - Electroactive metal complexes
  - Metal in cation is attracted toward cathode where electrodeposition takes place (not only diffusion, also electromigration)
- General formula of liquid metal salts:

$$\mathbf{M_aL_bY_cX_d}$$

  - M : metal ion
  - L : neutral ligand (e.g. *N*-alkylimidazole, acetonitrile)
  - Y : negatively charged ligand (e.g. Cl^-) often not present
  - X : counter anion (e.g. Tf_2N)

Liquid metal salts

- Tetrahedral metal ions with four ligands are analogues of tetraalkylammonium or phosphonium ions
- For example, copper(I) with four neutral ligands



- Choice of anion important for lowering the melting point
- Metal preferably in lowest available oxidation state
- Copper(I) prefers CN = 4
- First example: $[Cu(CH_3CN)_4][Tf_2N]$

Brooks et al., *Chem. Eur. J.* **17** (2011) 5054.

$[Cu(MeCN)_4][Tf_2N]$

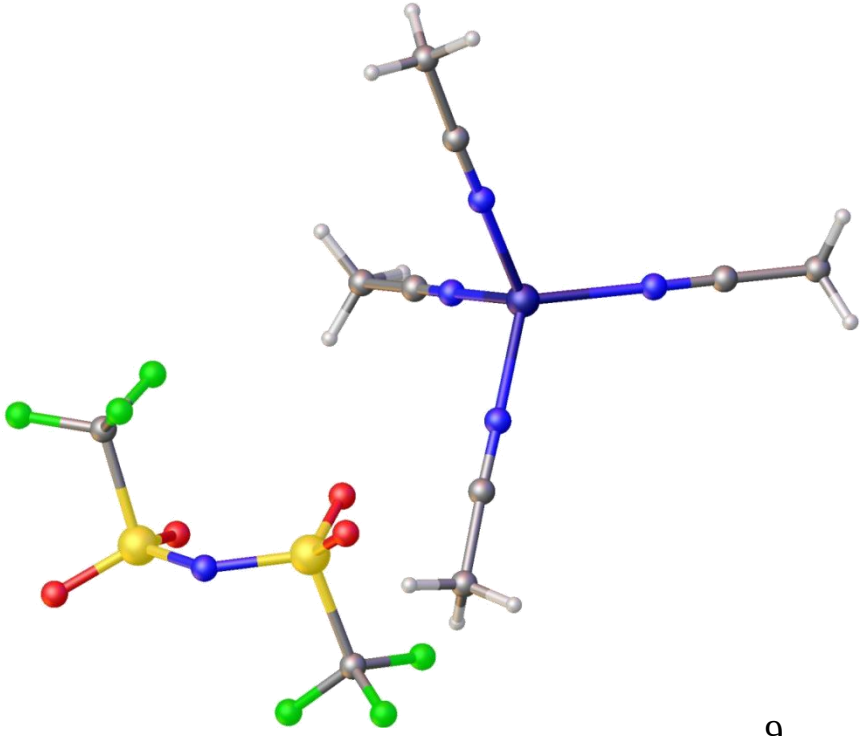
- Synthesis:

  $CuO + 2\ HTf_2N \rightarrow Cu(Tf_2N)_2 + H_2O$

  $Cu(Tf_2N)_2 + Cu + 8\ CH_3CN \rightarrow 2\ [Cu(CH_3CN)_4][Tf_2N]$

- Melting point: 66 °C
- For comparison:
  - $[NMe_4][Tf_2N]$ 133 °C
  - $[NEt_4][Tf_2N]$ 109 °C
  - $[NPr_4][Tf_2N]$ 105 °C

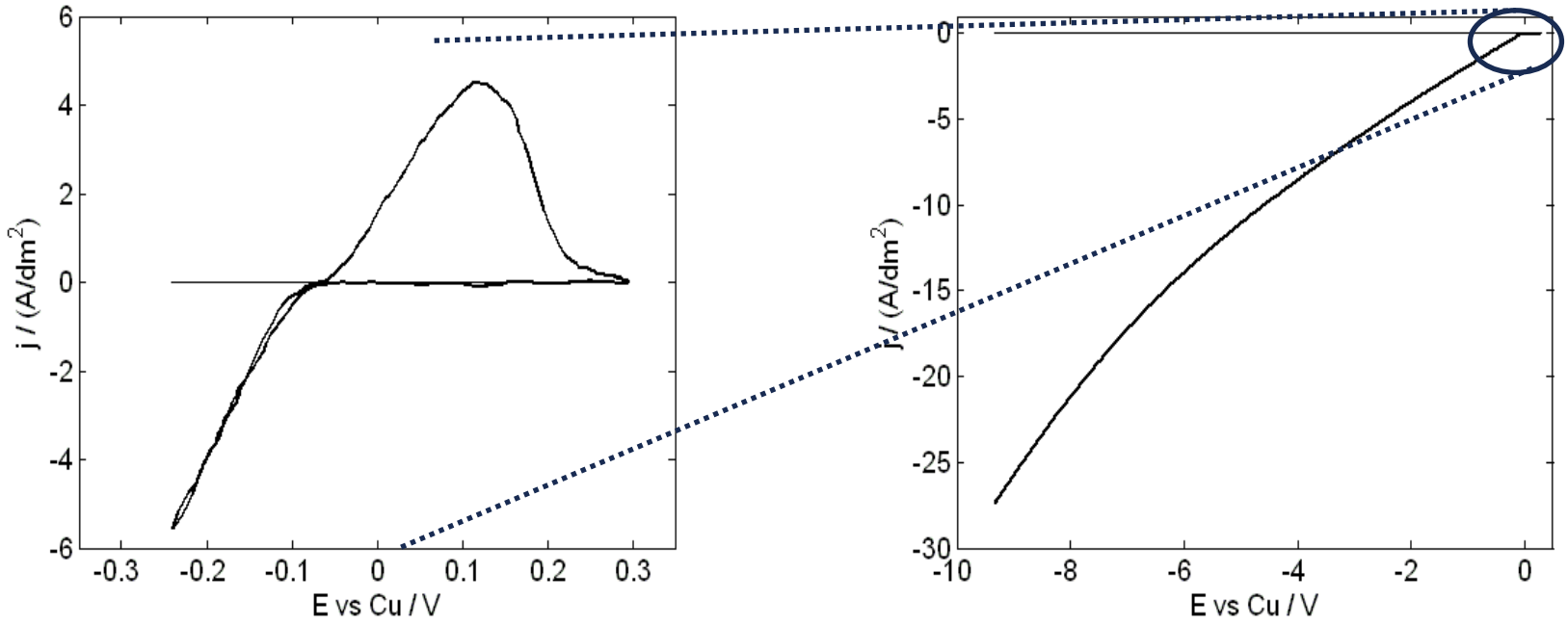
  - $[Cu(MeCN)_4][OTf]$ 124 °C



Brooks et al., *Chem. Eur. J.* **17** (2011) 5054.

Electrochemistry of $[Cu(MeCN)_4][Tf_2N]$

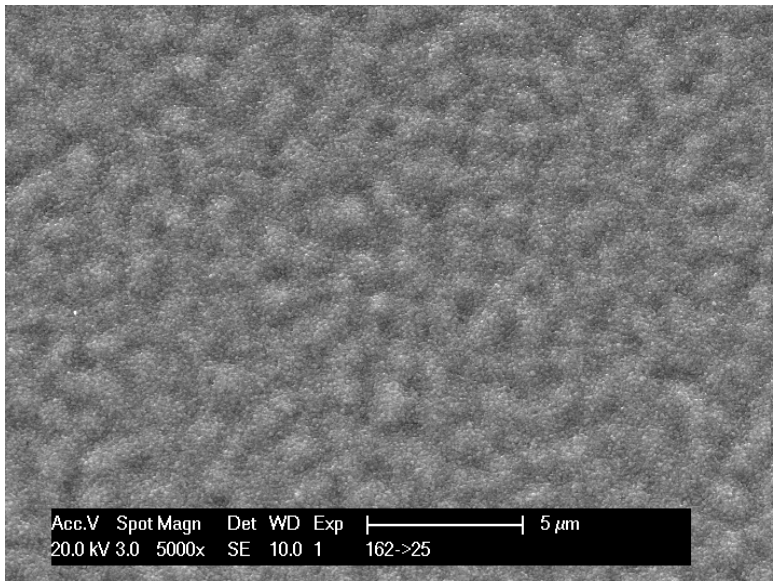
- Cathodic decomposition reaction of ionic liquid is reduction of metal ion to metallic state
- High current densities can be obtained
- Anodic reaction is stripping of copper from sacrificial electrode

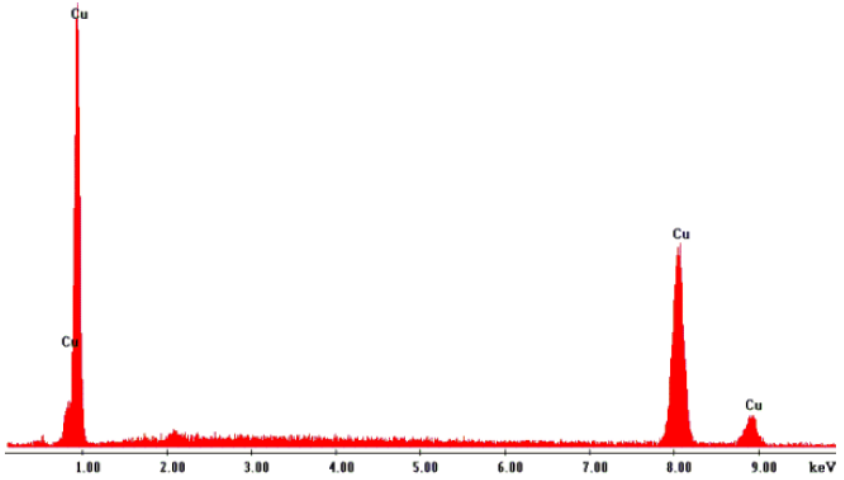


Brooks et al., *Chem. Eur. J.* **17** (2011) 5054.

Deposit from $[Cu(MeCN)_4][Tf_2N]$

- Current density: 25 $A.dm^{-2}$
- Deposit average thickness: 1 µm
- Time for deposit: 5 s



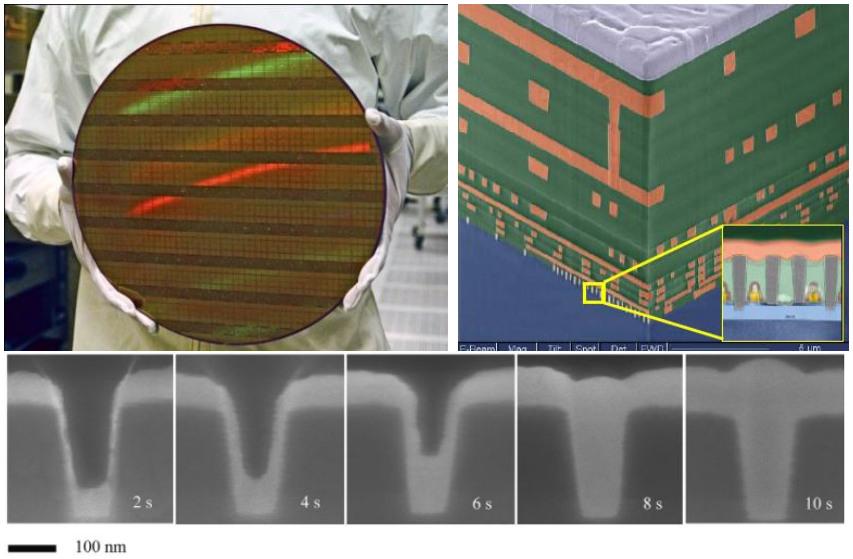


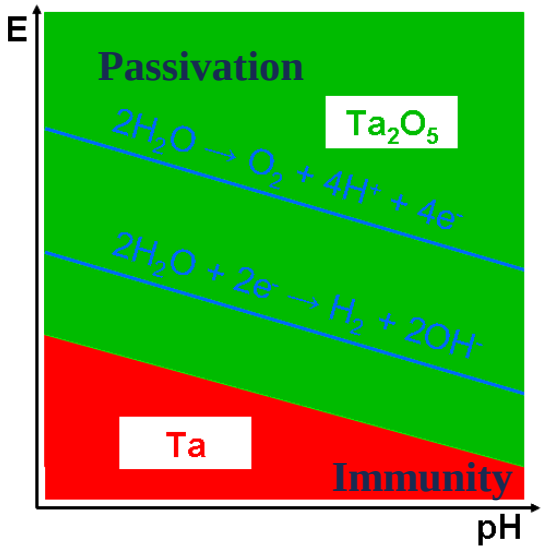
- EDX analysis shows no decomposition products included in layer

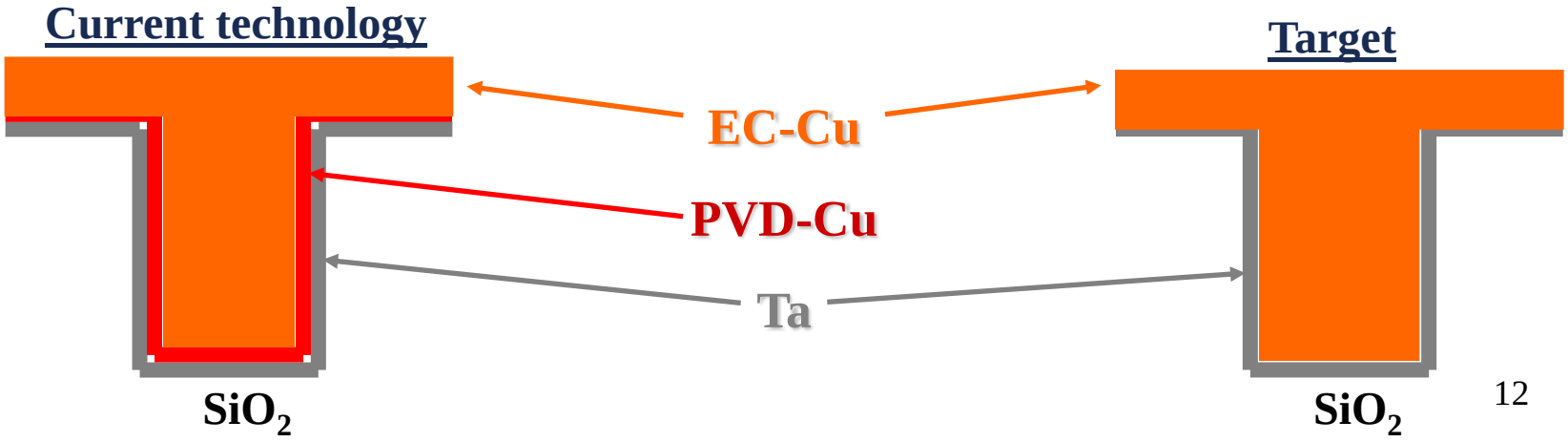
Brooks et al., *Chem. Eur. J.* **17** (2011) 5054.

Copper-on-tantalum plating

Motivation

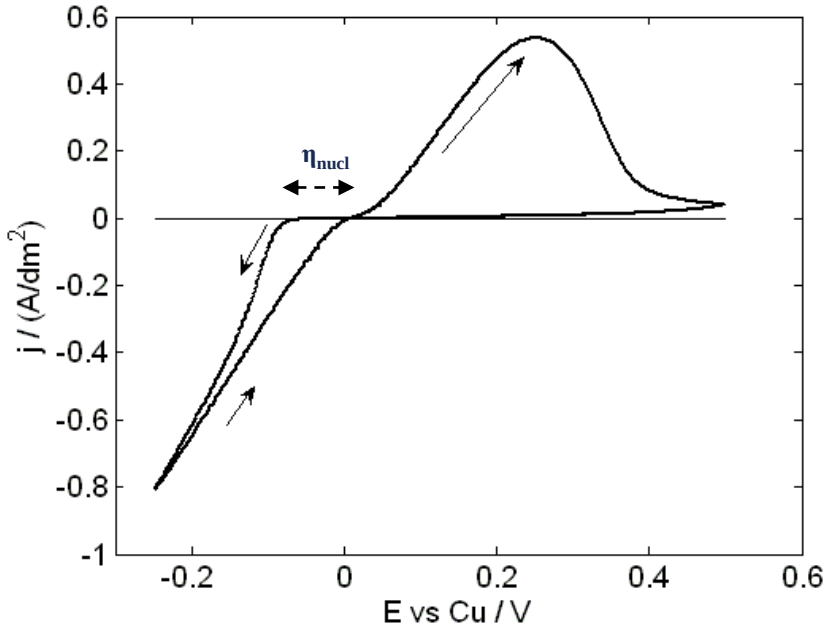


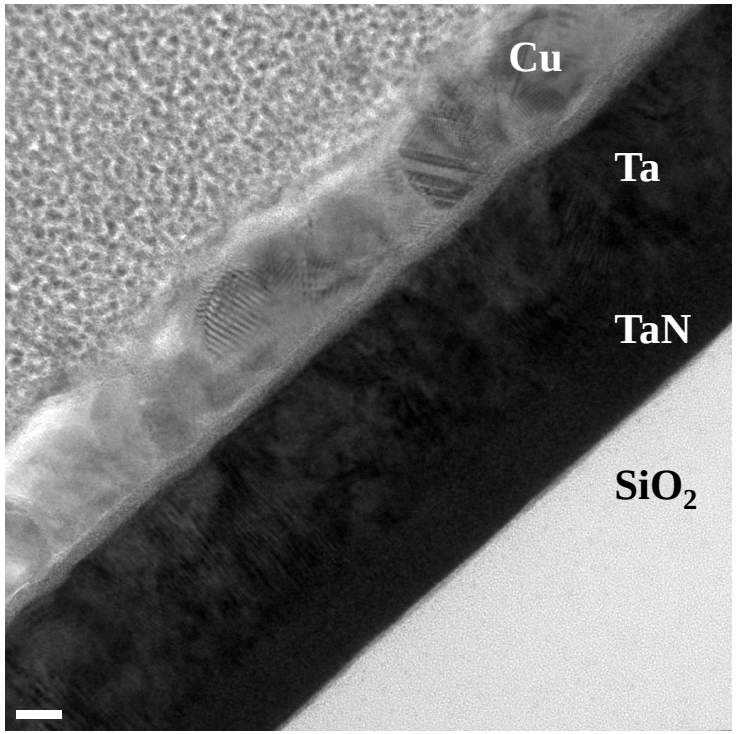




Copper-on-tantalum plating

- Cu-on-Ta from $[Cu(MeCN)_2][Tf_2N]$





Schaltin et al. *J. Electrochem. Soc.* **158** (2011) D647.

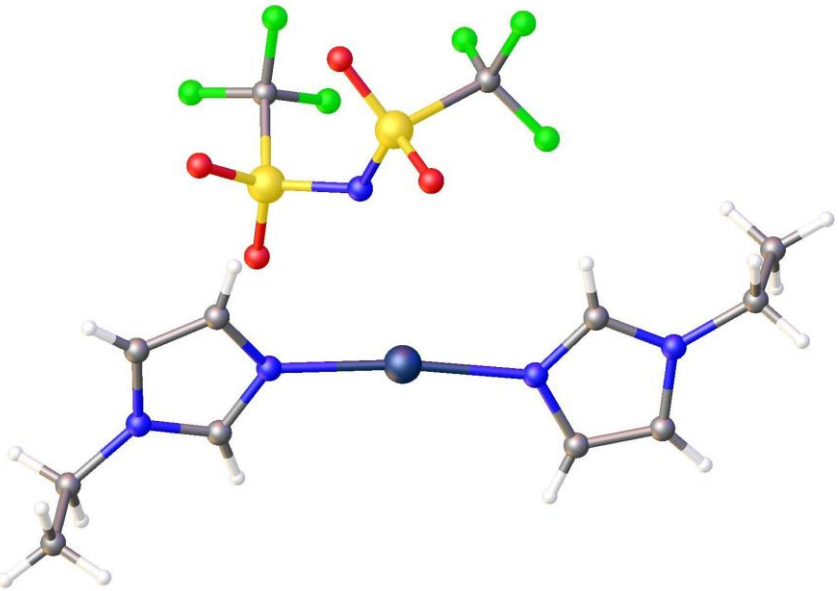
Silver complexes

- Silver(I) prefers CN = 2 or 3

- $Ag_2O + 2\ HTf_2N + 4\ MeCN \rightarrow 2\ [Ag(MeCN)_2][Tf_2N] + H_2O$

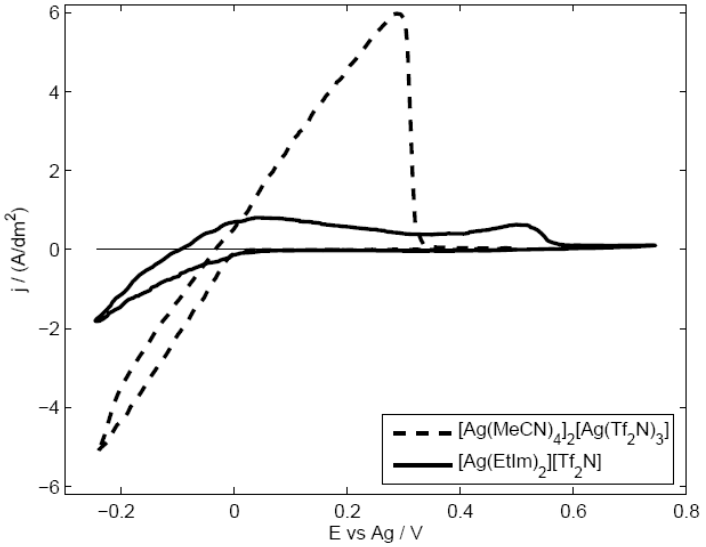
  m.p.: 18 °C

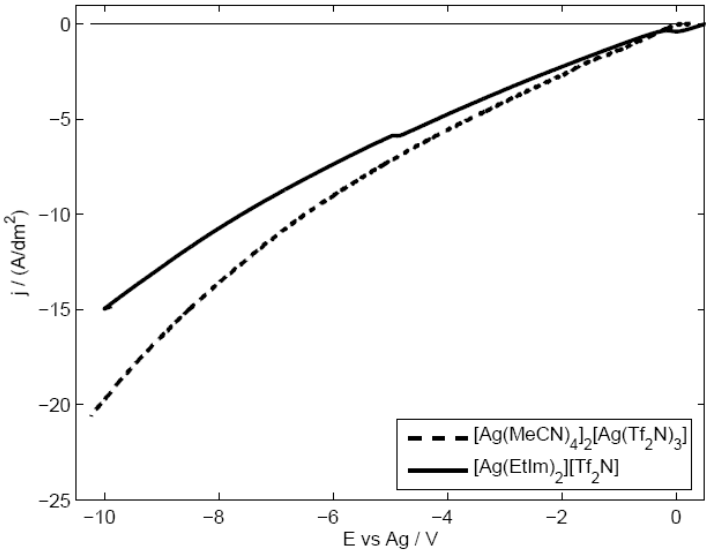
- $Ag(MeCN)_2Tf_2N + EtIm \rightarrow [Ag(EtIm)_2][Tf_2N]$ m.p.: 65 °C

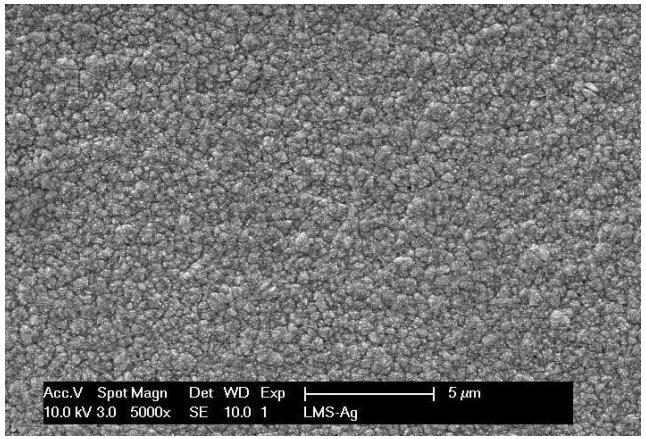


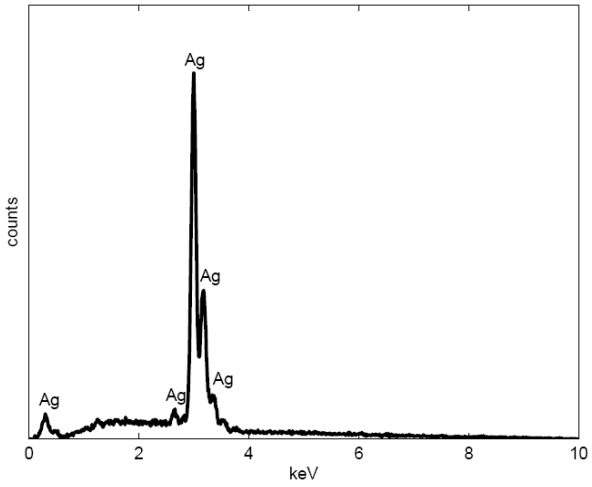
Schaltin et al. *PCCP* **14** (2012) 1706.

Deposition of silver



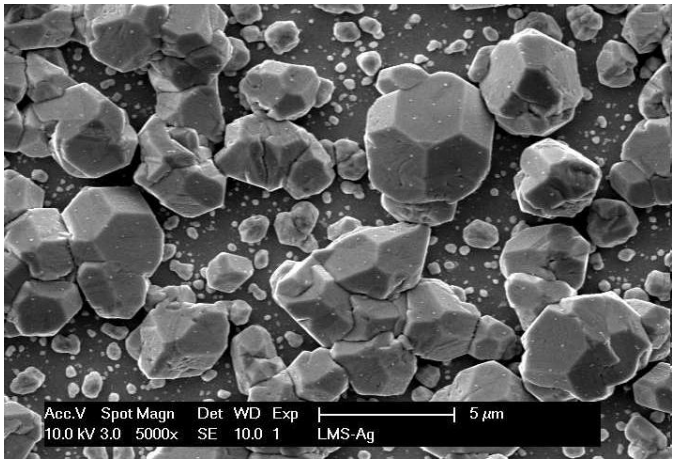




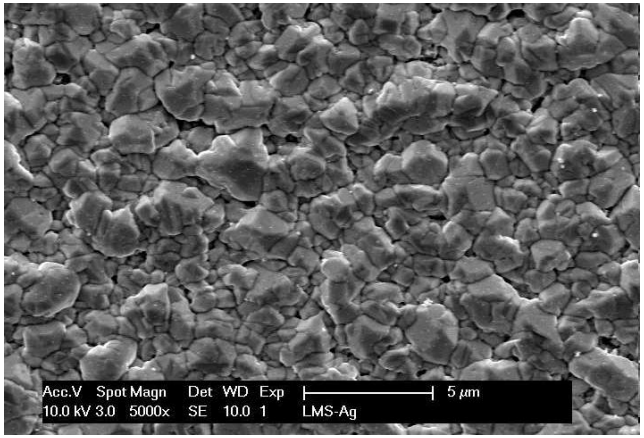


Schaltin et al. *PCCP* **14** (2012) 1706.

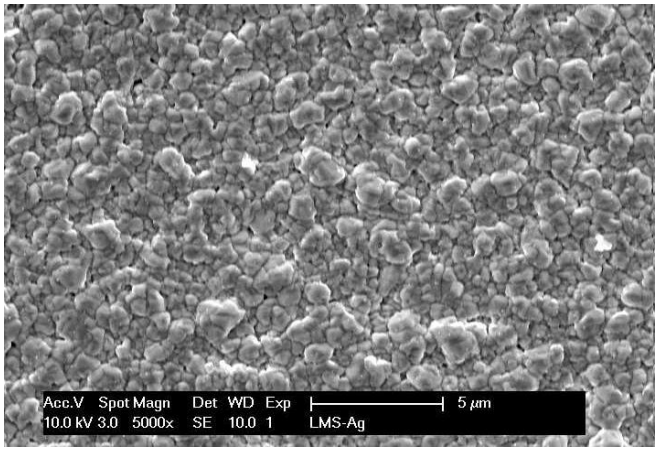
Silver deposits: influence of current density



1 A dm^{-2}



5 A dm^{-2}



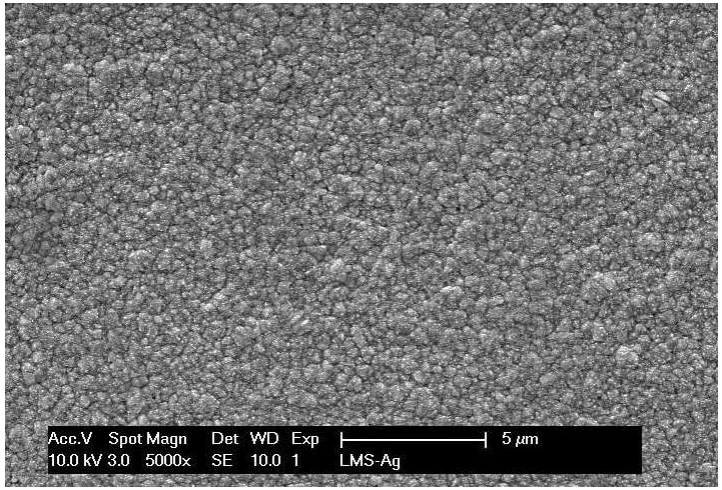
25 A dm^{-2}

$[Ag(MeCN)_4]_2[Ag(Tf_2N)_3]$

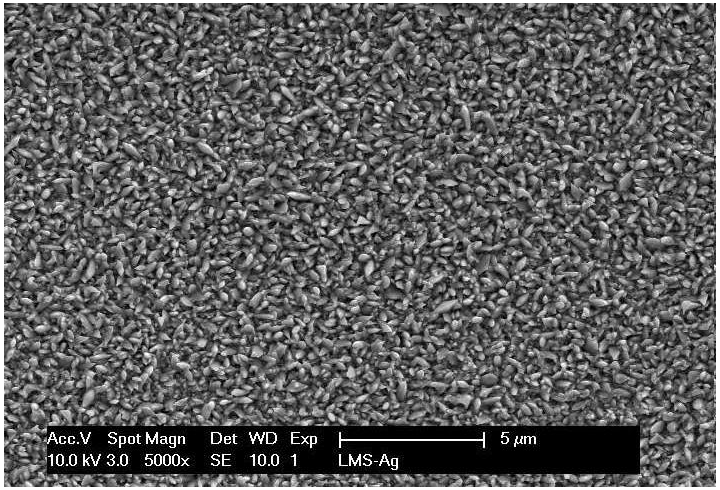
Au working electrode
50 °C
Theoretical thickness: 1 µm

Schaltin et al. *PCCP* **14** (2012) 1706.

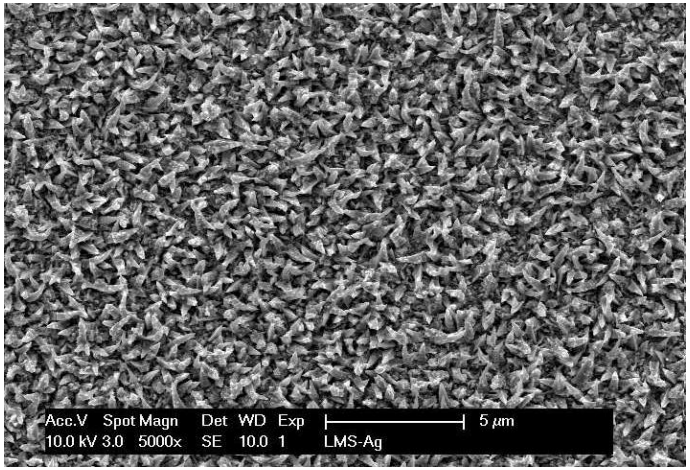
Silver deposits: influence of current density



1 A dm^{-2}



5 A dm^{-2}



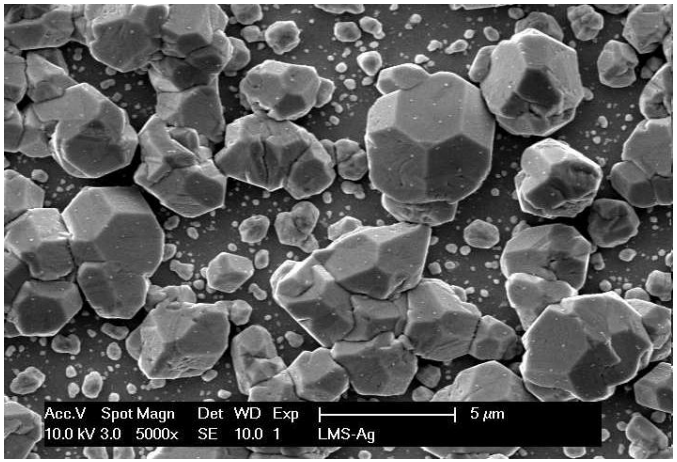
25 A dm^{-2}

$[Ag(EtIm)_2][Tf_2N]$

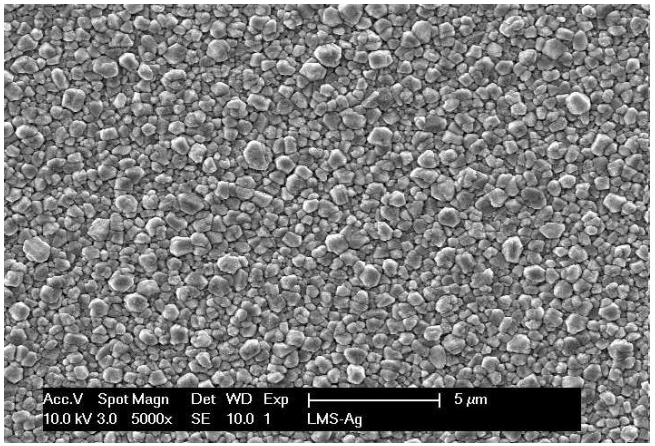
Au working electrode
90 °C
Theoretical thickness: 1 µm

Schaltin et al. *PCCP* **14** (2012) 1706.

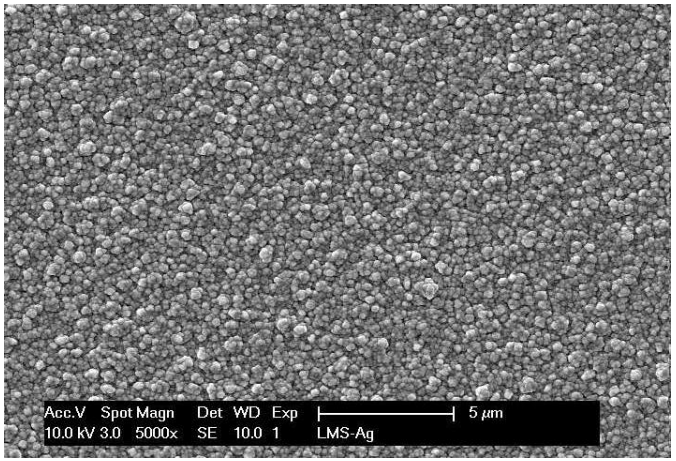
Silver deposits: influence of additives



No additive



Thiourea (0.05 M)



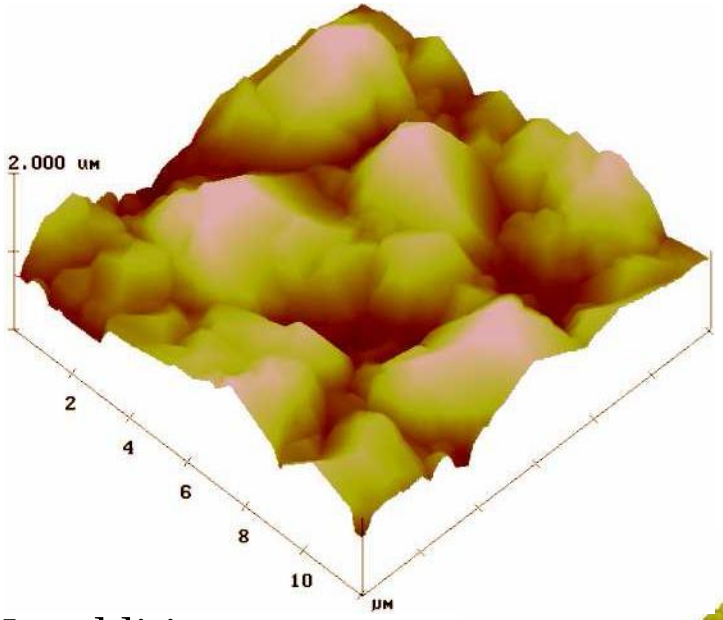
1*H*-benzotriazole (0.05 M)

$[Ag(MeCN)_4]_2[Ag(Tf_2N)_3]$

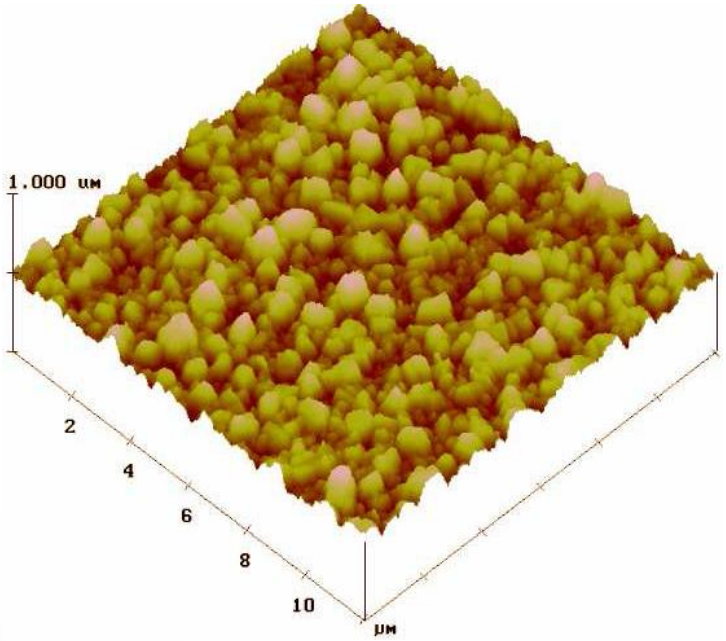
Au working electrode
50 °C, 1 A dm^{-2}
Theoretical thickness: 1 μm

Schaltin et al. *PCCP* **14** (2012) 1706.

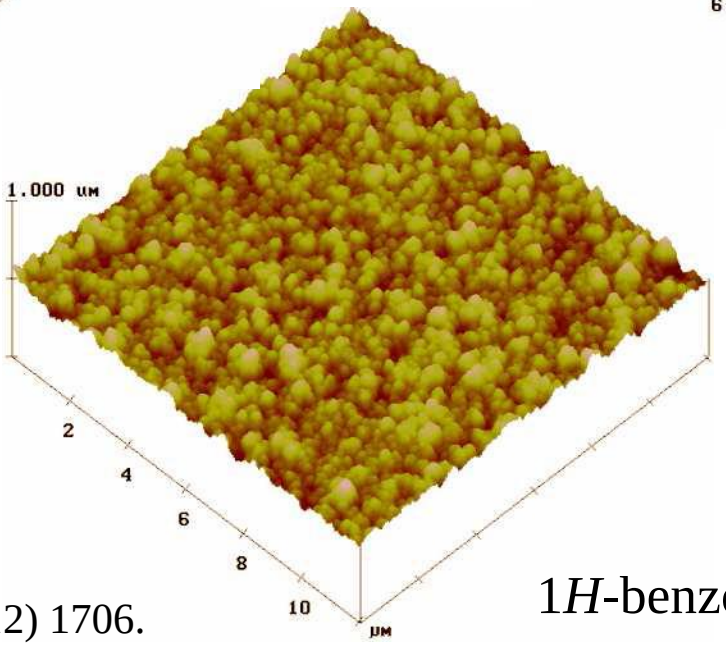
Silver deposits: influence of additives (AFM)



No additive



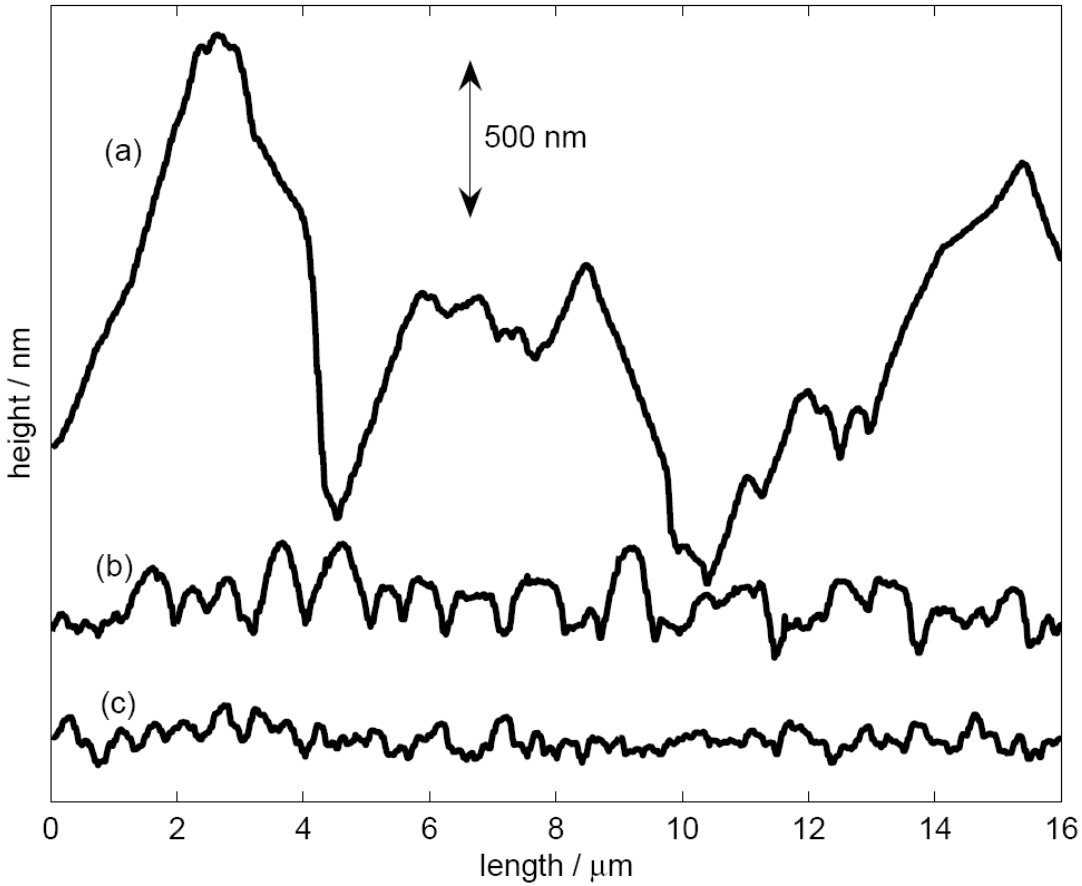
Thiourea (0.05 M)



1*H*-benzotriazole (0.05 M)

Schaltin et al. *PCCP* **14** (2012) 1706.

Silver deposits: influence of additives (AFM)

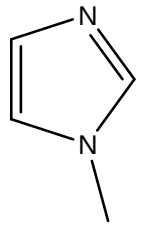


Roughness profiles
(a) No additive; (b) thiourea (0.05 M);
(c)1*H*-benzotriazole (0.05 M)

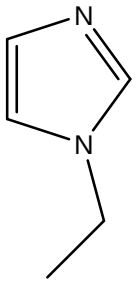
Schaltin et al. *PCCP* **14** (2012) 1706.

N-alkylimidazole silver liquid metal salts

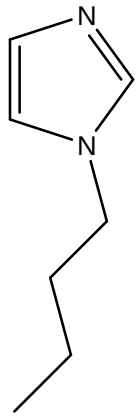
- Liganden:



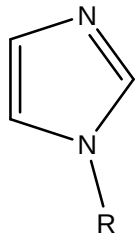
MeIm



EtIm

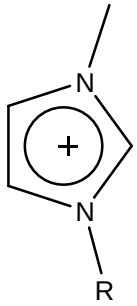


BuIm



Rim (R = He, Oc, De, Do)

- Notice: these ligands are the precursors for the 1,3-dialkylimidazolium ionic liquids

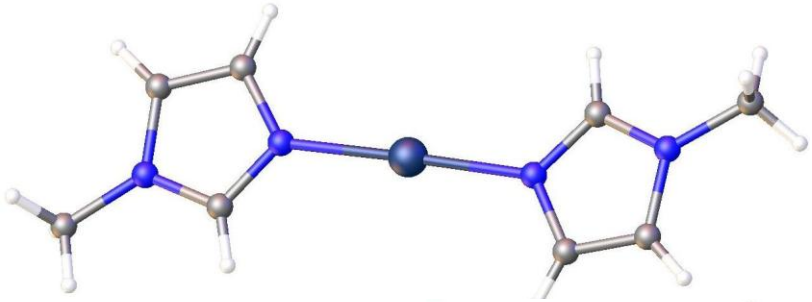


Brooks et al., *Dalton Trans.* **41** (2012) 6902.

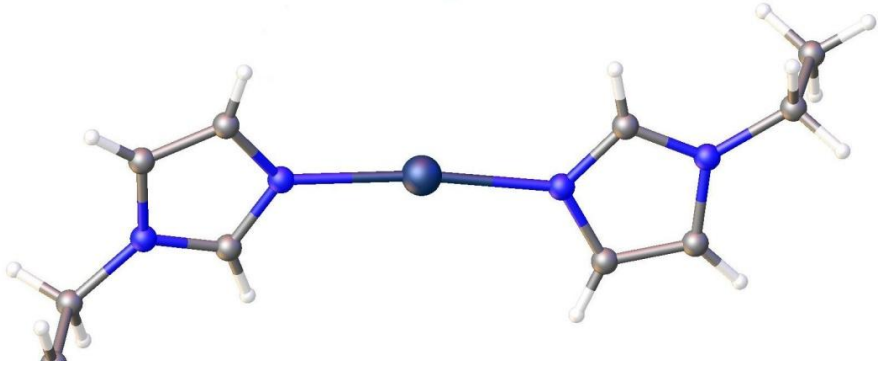
N-Alkylimidazole silver liquid metal salts

$[Ag(MeCN)_2][Tf_2N] + 2\ RIm \rightarrow [Ag(RIm)_2][Tf_2N]$

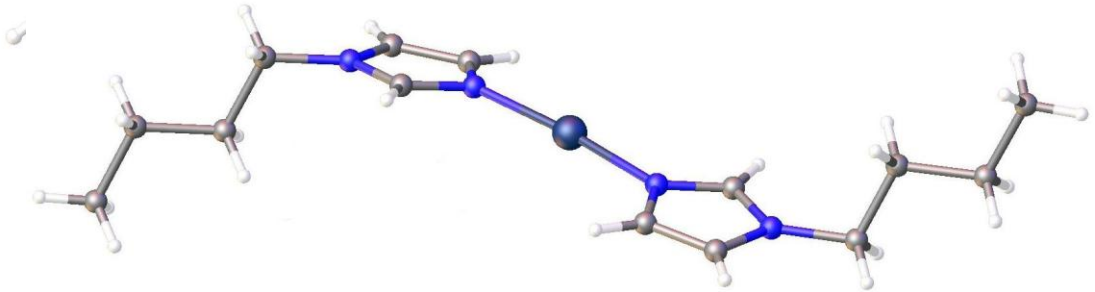
$[Ag(MeIm)_2][Tf_2N]$
m.p. = 87 °C



$[Ag(EtIm)_2][Tf_2N]$
m.p. = 65 °C



$[Ag(BuIm)_2][Tf_2N]$
m.p. = 42 °C



Longer chains give lower melting points

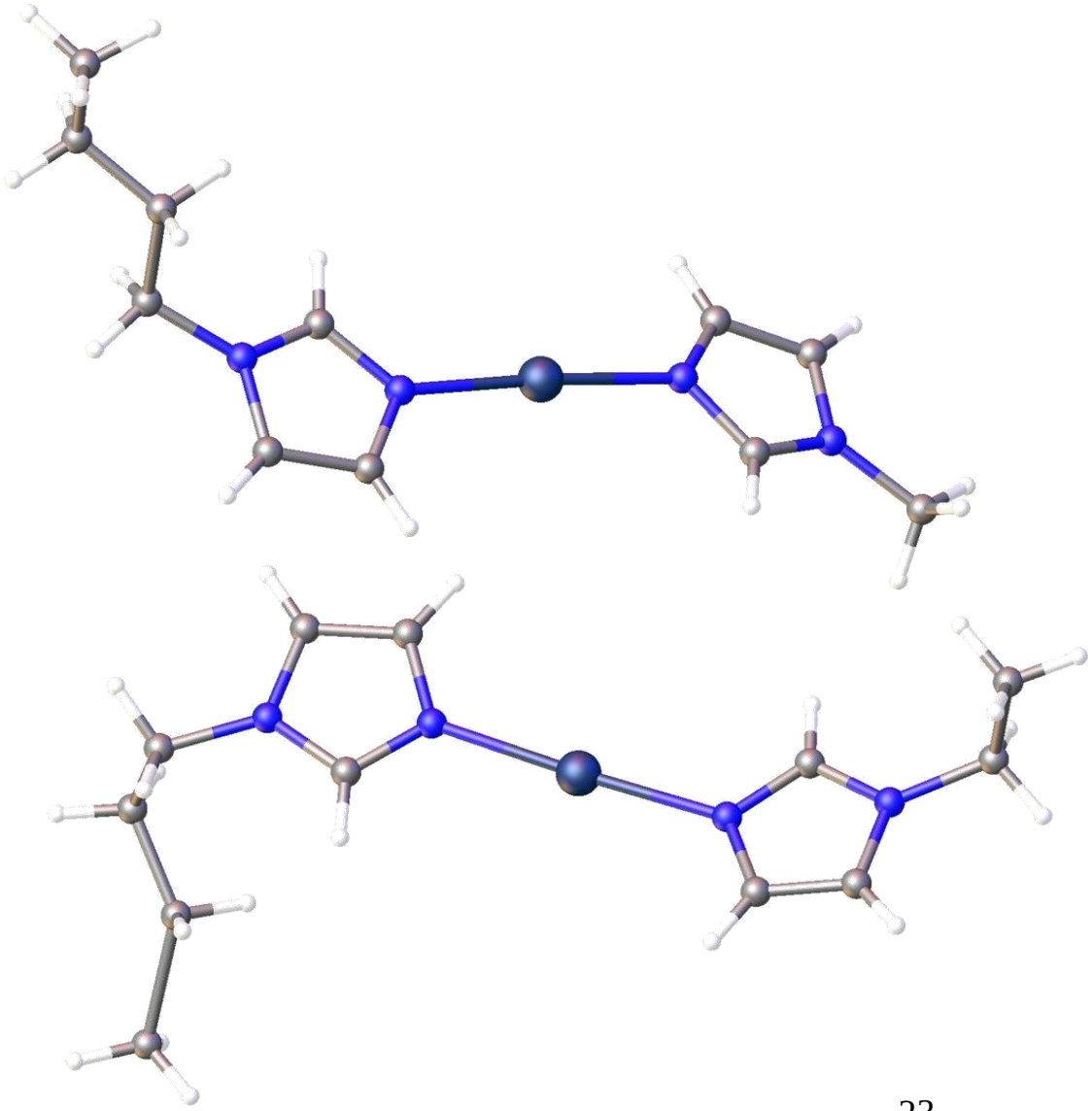
Brooks et al., *Dalton Trans.* **41** (2012) 6902.

Heteroleptic silver complexes: 2 different ligands

[Ag(MeIm)(EtIm)][Tf_2N]
m.p. = 35 °C

[Ag(MeIm)(BuIm)][Tf_2N]
m.p. = 30 °C

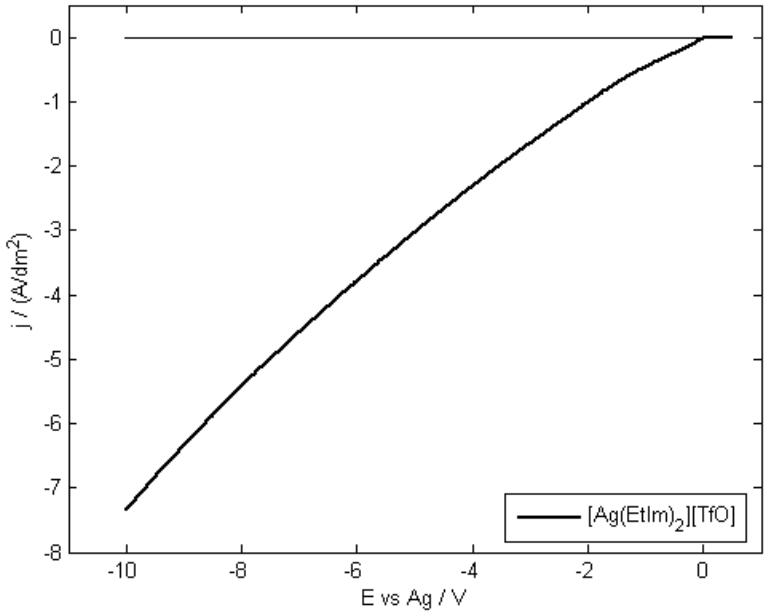
[Ag(EtIm)(BuIm)][Tf_2N]
m.p. = 27 °C



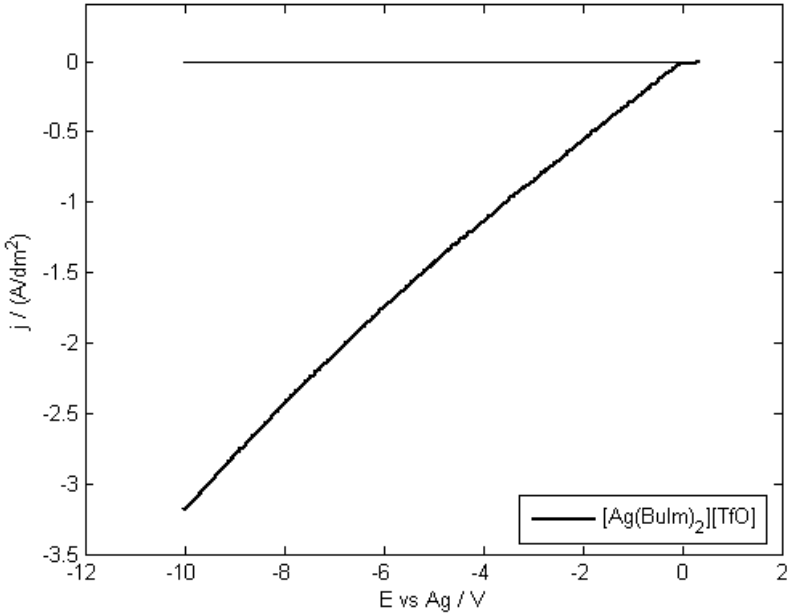
Asymmetry gives lower melting points

Brooks et al., *Dalton Trans.* **41** (2012) 6902.

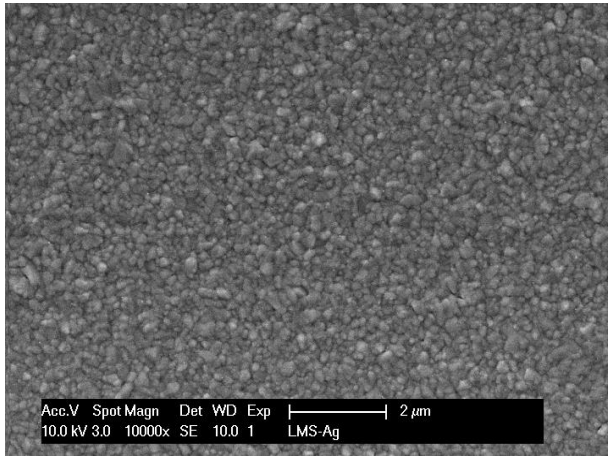
Deposition of silver from $[Ag(EtIm)_2][OTf]$ and $[Ag(BuIm)_2][OTf]$



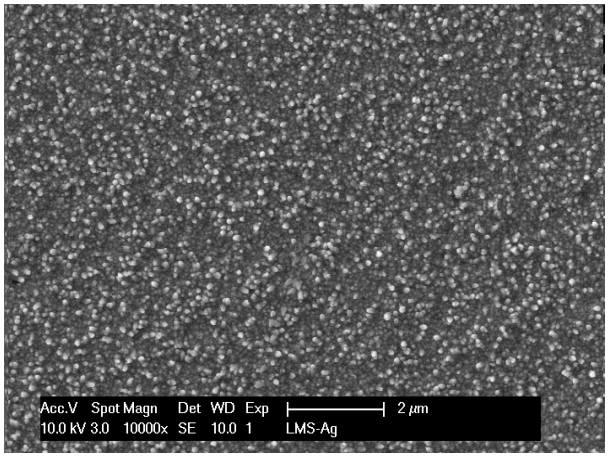
$[Ag(EtIm)_2][OTf]$



$[Ag(BuIm)_2][OTf]$



Deposits at 90 °C and
1 A dm^{-2}

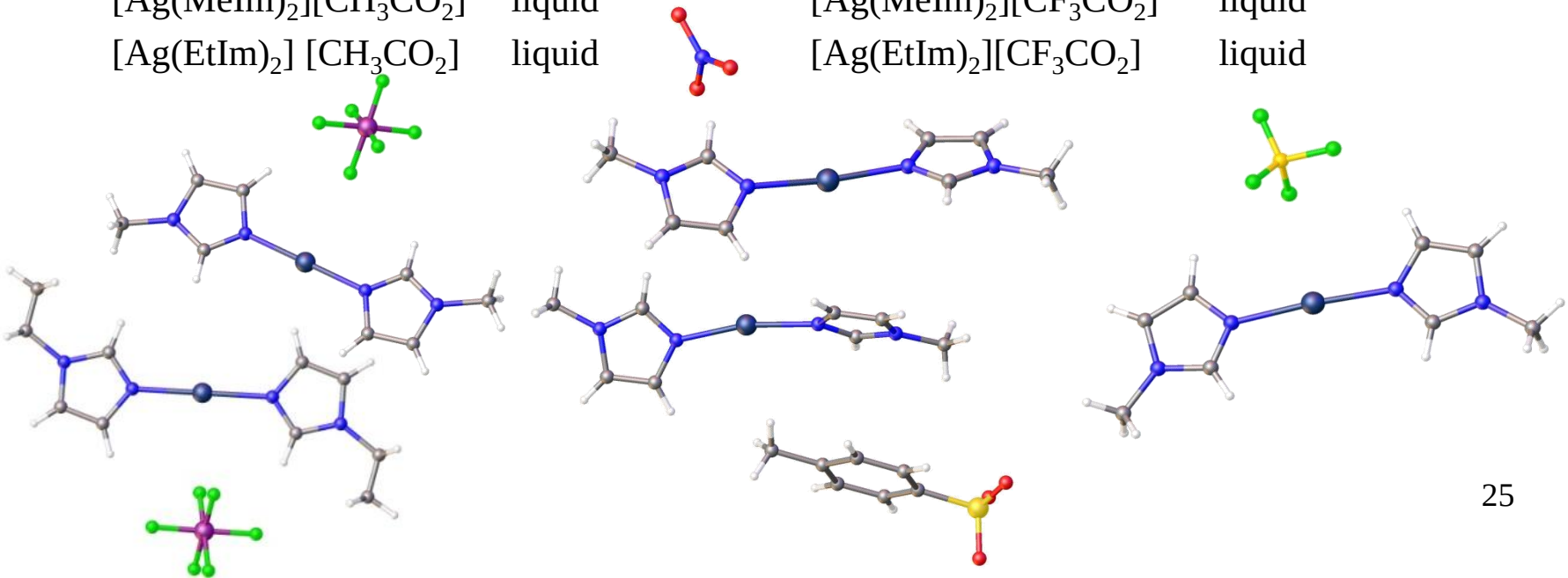


Silver salts with different anions – PF_6, BF_4, NO_3, tosylate, CH_3CO_2, CF_3CO_2

$[Ag(MeIm)_2][PF_6]$	115 °C	$[Ag(MeIm)_2][BF_4]$	101 °C
$[Ag(EtIm)_2][PF_6]$	83 °C	$[Ag(EtIm)_2][BF_4]$	liquid
$[Ag(MeIm)(EtIm)][PF_6]$	50 °C	$[Ag(MeIm)(EtIm)][BF_4]$	54 °C

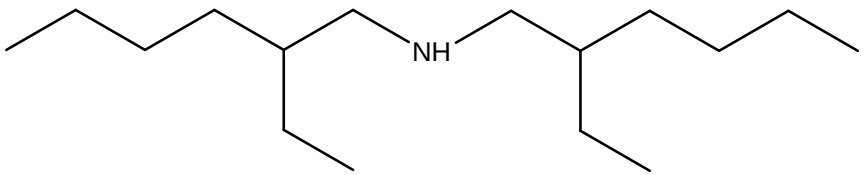
$[Ag(MeIm)_2][NO_3]$	**86 °C**	$[Ag(MeIm)_2][OTs]$	115 °C
$[Ag(EtIm)_2][NO_3]$	**liquid**	$[Ag(EtIm)_2][OTs]$	liquid
$[Ag(MeIm)(EtIm)][NO_3]$	**liquid**		

$[Ag(MeIm)_2][CH_3CO_2]$	liquid	$[Ag(MeIm)_2][CF_3CO_2]$	liquid
$[Ag(EtIm)_2]\ [CH_3CO_2]$	liquid	$[Ag(EtIm)_2][CF_3CO_2]$	liquid

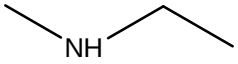


Silver liquid metal salts with amine ligands

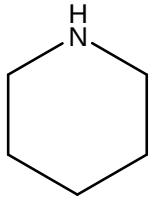
- Secondary amine ligands



Di-2-EtHexAm



EtDiAm

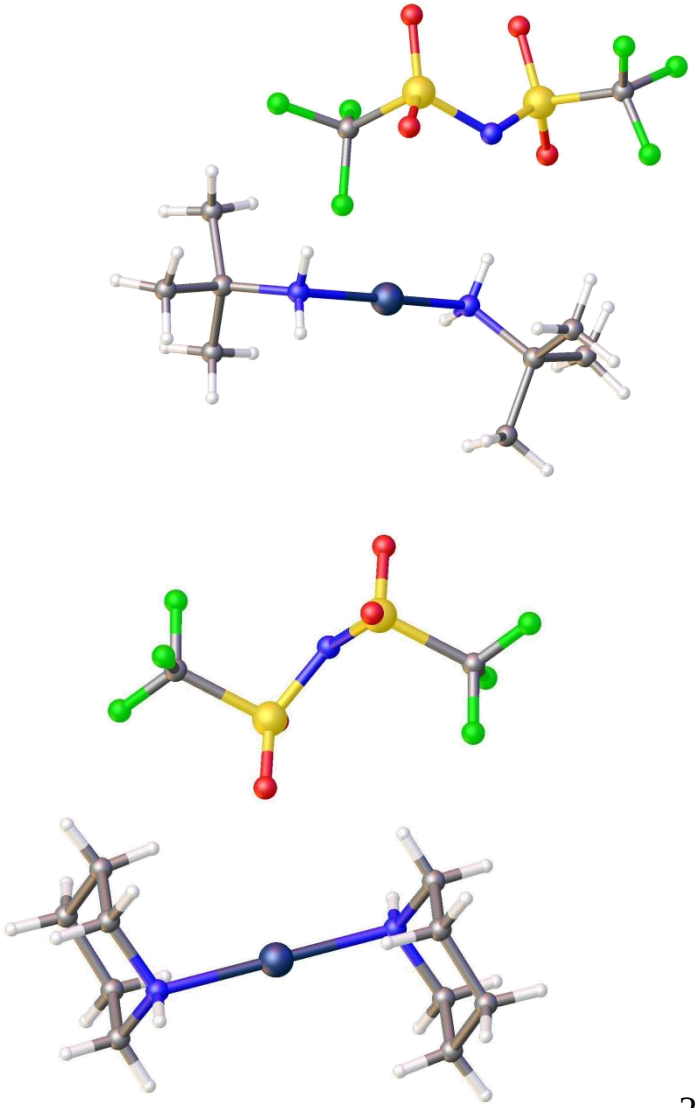


piperidine

Depuydt et al. *ChemSusChem* **78** (2013) 578.

Silver liquid metal salts with amine ligands

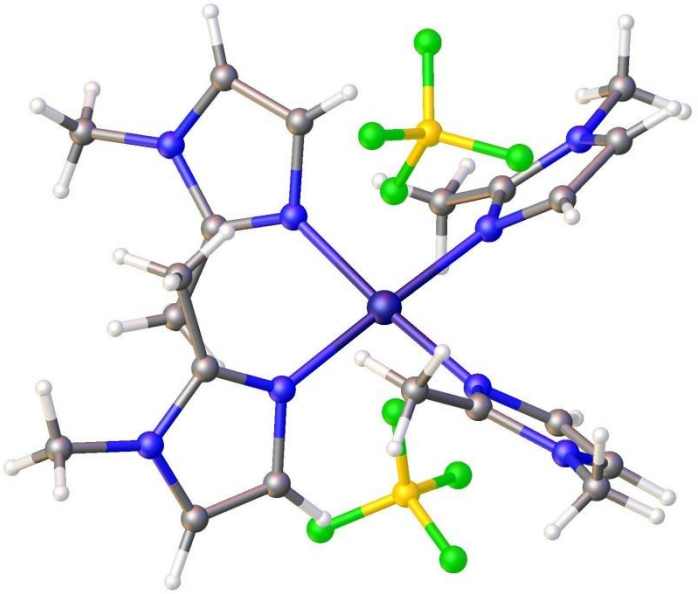
$[Ag(EtAm)_2][Tf_2N]$	liquid
$[Ag(PrAm)_2][Tf_2N]$	liquid
$[Ag(sec\text{-}BuAm)_2][Tf_2N]$	liquid
$[Ag(iso\text{-}BuAm)_2][Tf_2N]$	31 °C
$[Ag(t\text{-}BuAm)_2][Tf_2N]$	62 °C
$[Ag(2\text{-}EtHexAm)_2][Tf_2N]$	5 °C
$[Ag(Di\text{-}2\text{-}EtHexAm)_2][Tf_2N]$	liquid
$[Ag(piperidine)_2][Tf_2N]$	100 °C
$[Ag(EtDiAm)][Tf_2N]$	171 °C
$[Ag(EtDiAm)_2][Tf_2N]$	21 °C

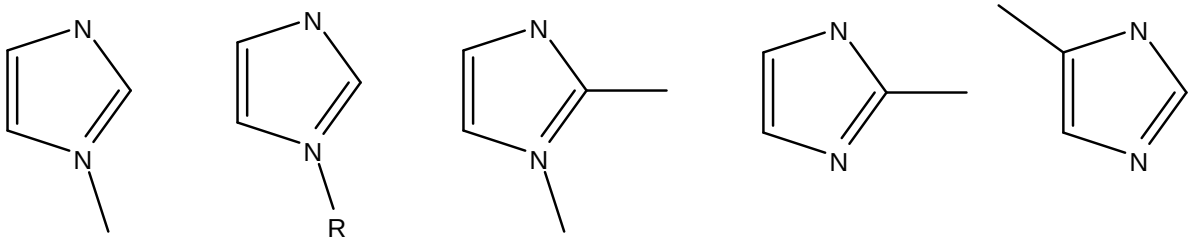


Depuydt et al. *ChemSusChem* **78** (2013) 578.

Copper(II)-containing Liquid Metal Salts

$[Cu(MeIm)_6][Tf_2N]_2$	50 °C
$[Cu(BuIm)_4][Cl]_2$	55 °C
$[Cu(BuIm)_4][Tf_2N]_2$	**< RT**
$[Cu(BuIm)_4][NO_3]_2$	126 °C
$[Cu(HexIm)_4][Cl]_2$	66 °C
$[Cu(MeIm)_6][Tf_2N]_2$	50 °C
$[Cu(1,2\text{-}DiMeIm)_4][BF_4]_2$	185 °C



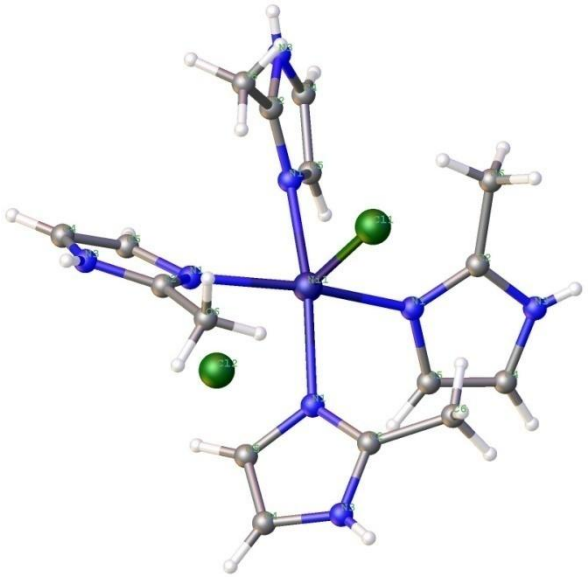


R = Bu,Hex

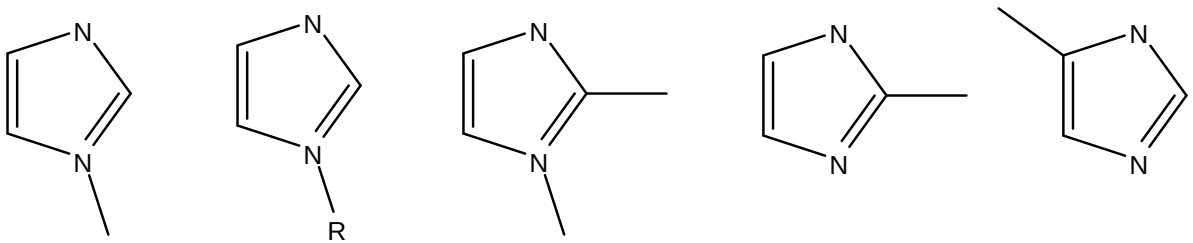
MeIm, BuIm, HexIm 1,2-DiMeIm 2-MeIm 4-MeIm

Liquid Metal Salts of other transition metals

$[Ni(2\text{-}MeIm)_4Cl][Cl]$	83 °C
$[Ni(BuIm)_6][Cl]_2$	124 °C
$[Ni(HexIm)_6][Cl]_2$	69 °C
$[Co(HexIm)_6][Cl]_2$	**34 °C**
$[Fe(MeIm)_6][NO_3]_2$	60 °C
$[Mn(BuIm)_6][Cl]_2$	58 °C
$[Mn(HexIm)_6][Cl]_2$	**45 °C**



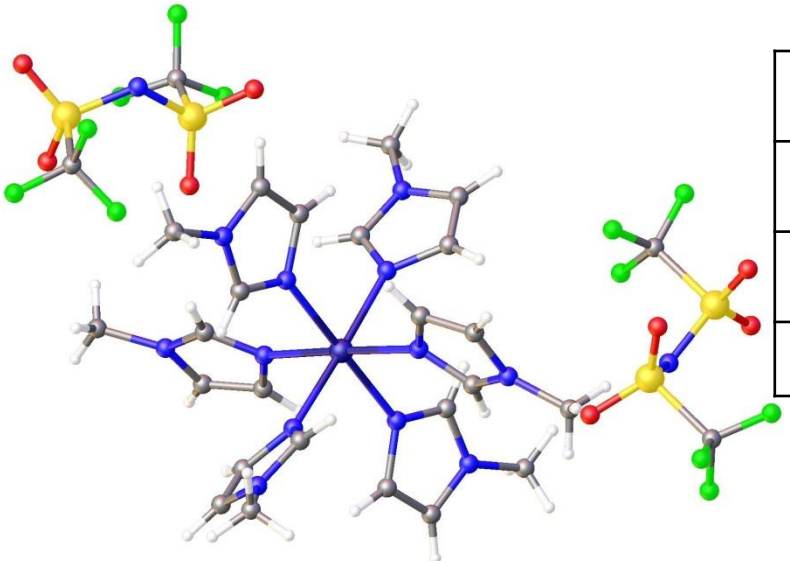
$[Ni(2\text{-}MeIm)_4Cl][Cl]$ 83 °C



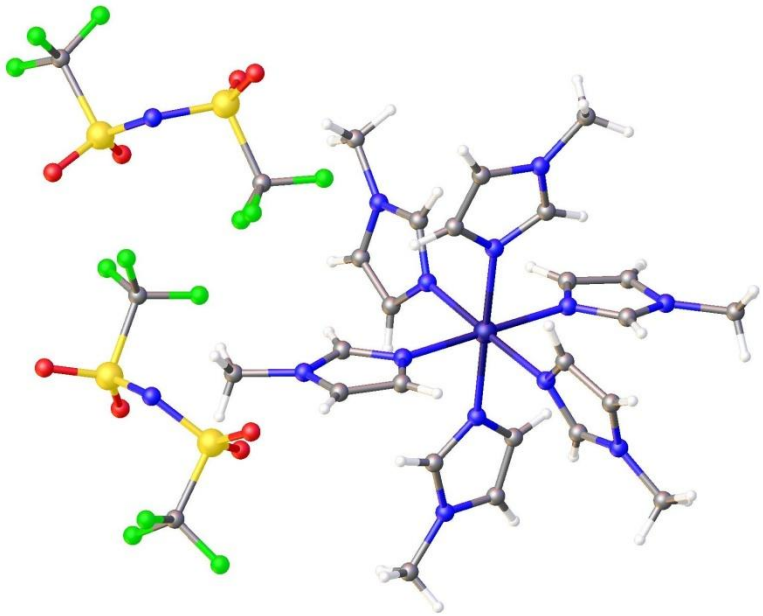
R = Bu,Hex

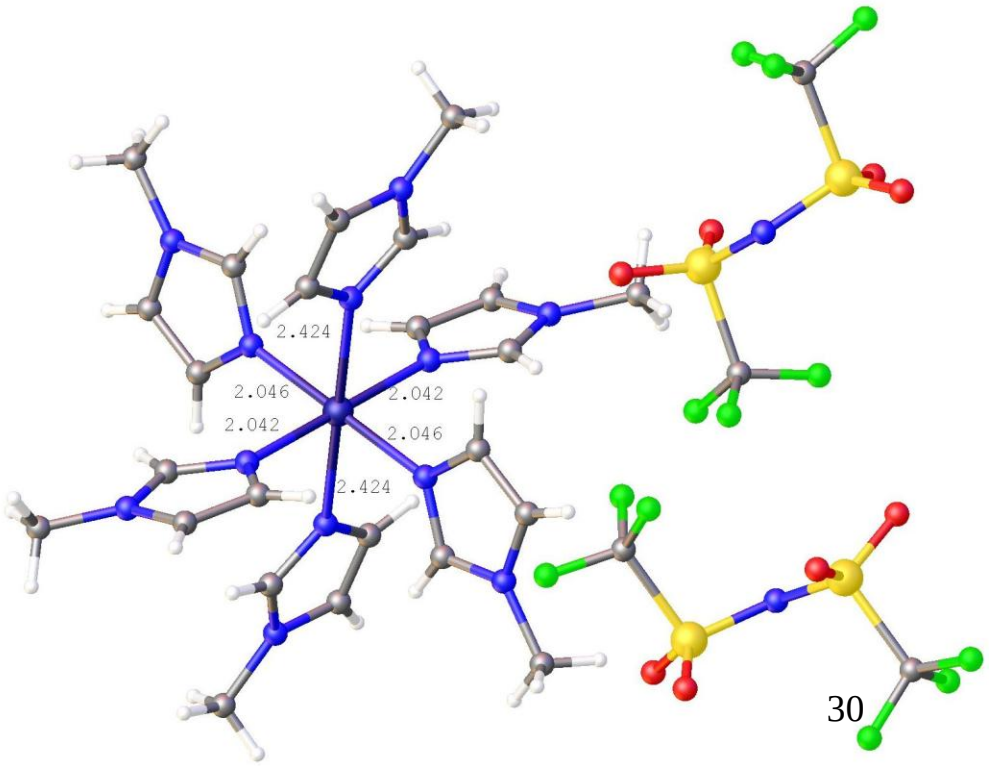
MeIm, BuIm, HexIm 1,2-DiMeIm 2-MeIm 4-MeIm

Effect of metal ion: Co/Ni/Cu (Jahn-Teller effect)



Compound	m.p. (°C)	Cu-N distances
$[Co(MeIm)_6][Tf_2N]_2$	137	6 × 2.15 Å
$[Ni(MeIm)_6][Tf_2N]_2$	147	6 × 2.12 Å
$[Cu(MeIm)_6][Tf_2N]_2$	50	4 × 2.04 Å, 2 × 2.42 Å

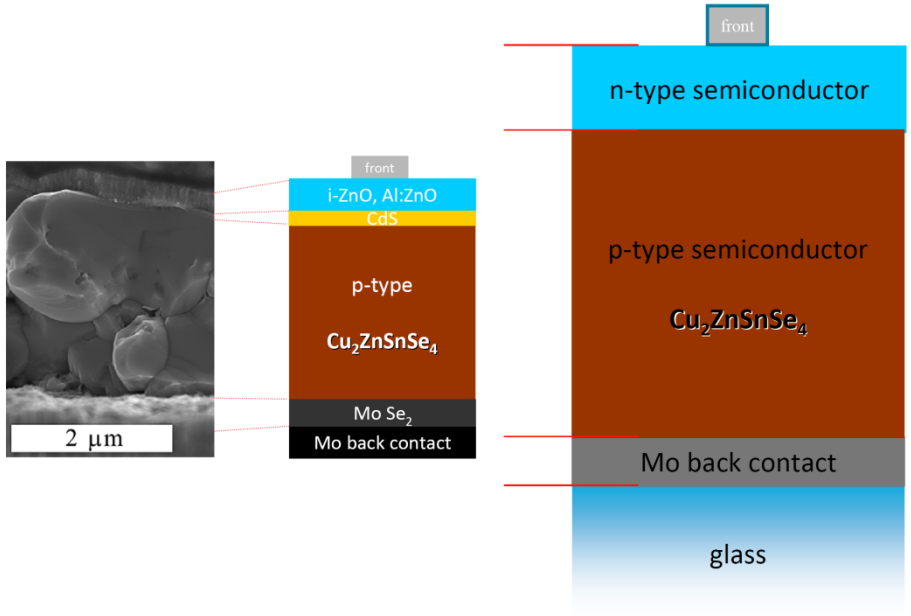


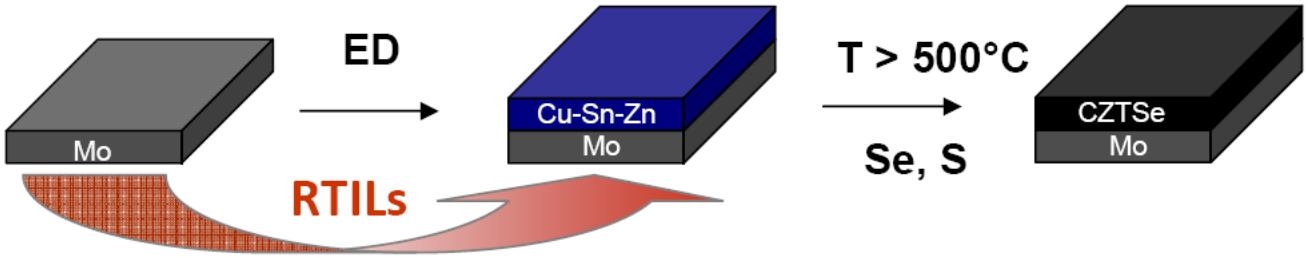


Precursors for kesterite-based thin film solar cells

Kesterite absorbers
$Cu_2ZnSn(S,Se)_4$

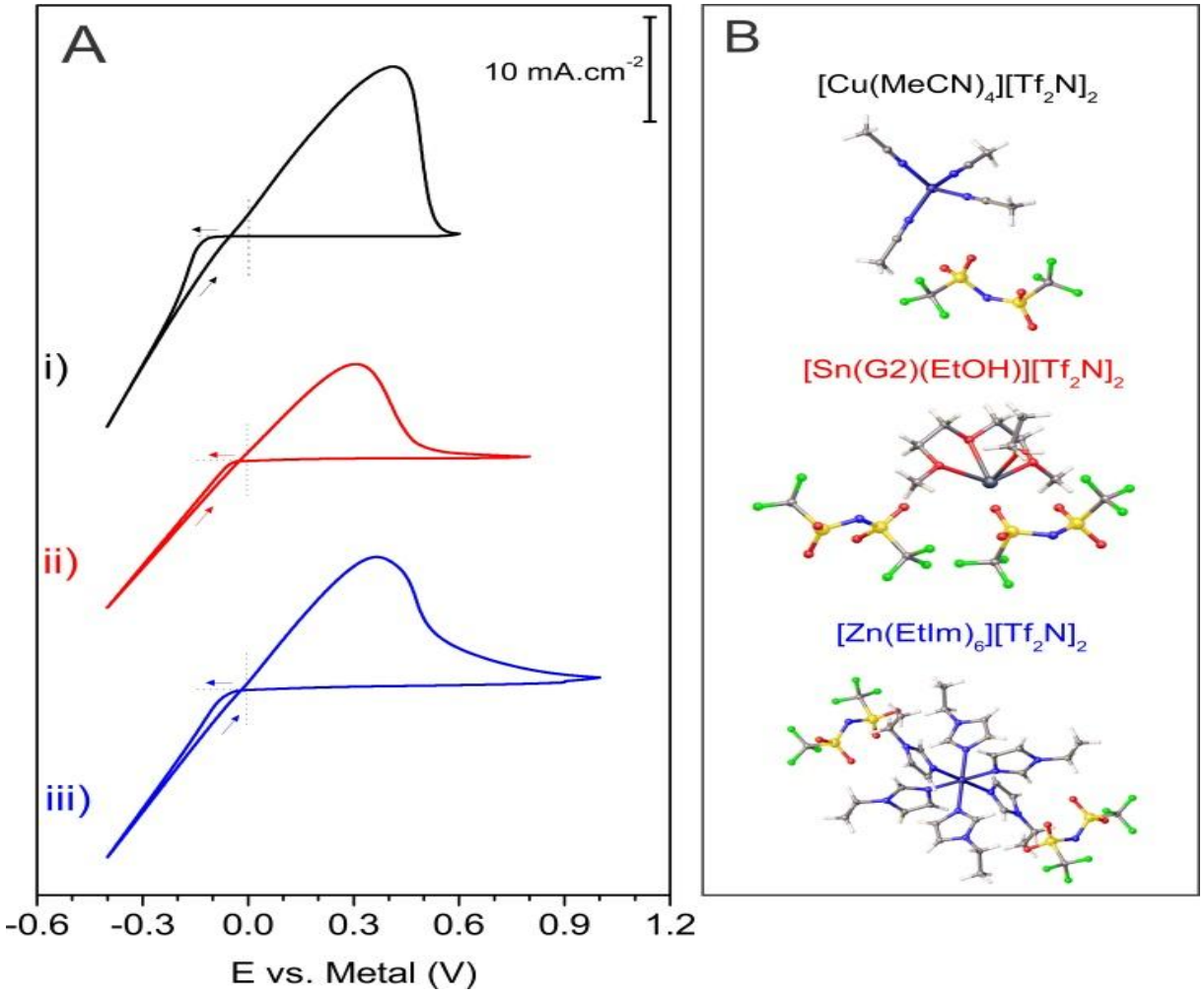
- abundant metals
- p-type semiconductors
- high absorption coefficient
- direct band gap (0.9 – 1.5 eV)





Collaboration with University of Luxemburg (Steichen/Dale)

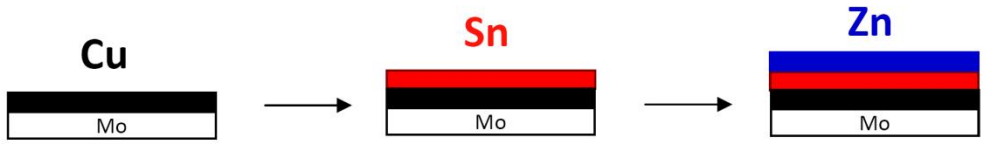
Electrodeposition of Cu/Sn/Zn stacks



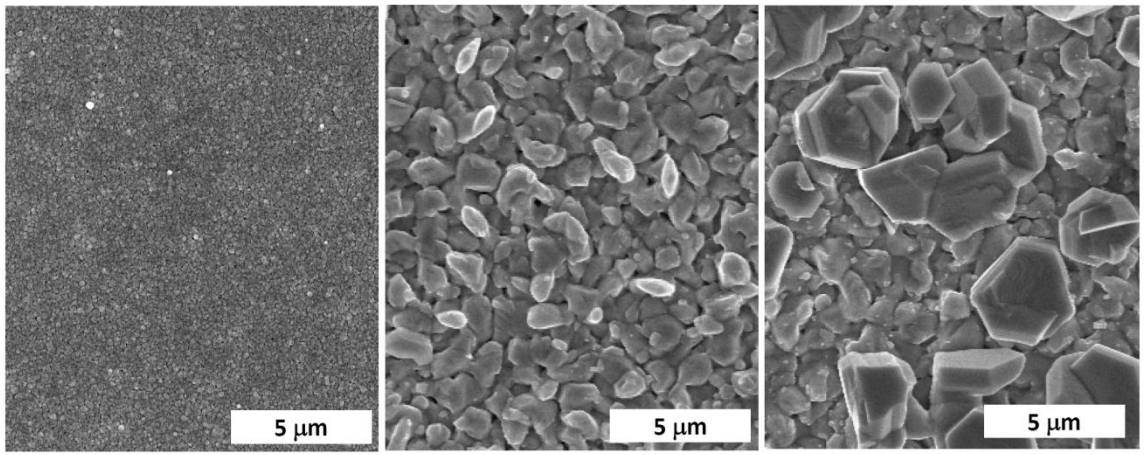
Collaboration with University of Luxembourg (Steichen/Dale)

Electrodeposition of Cu/Sn/Zn stacks

Selected LMS	η / mPa.s	t_{dep} / s	plat. eff. / %
$[Cu(MeCN)_4][Tf_2N]$	9 (± 1)	**3.0 - 3.5**	95 (± 5)
$[Sn(G2)(EtOH)][Tf_2N]_2$	29 (± 4)	**3.5 - 4.0**	69 (± 6)
$[Zn(EtIm)_6][Tf_2N]_2$	12 (± 2)	**3.5 - 4.0**	89 (± 6)



90 ° C



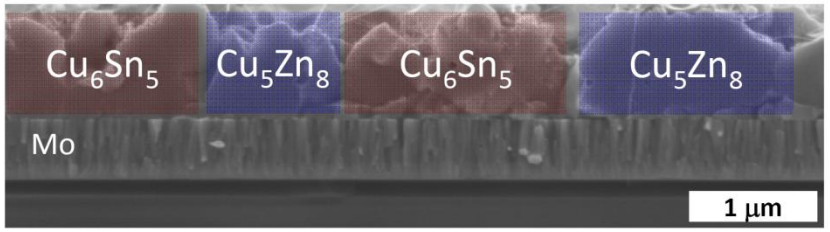
Collaboration with University of Luxembourg (Steichen/Dale)

Total ED time < 12 s !

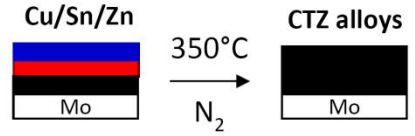
Conversion of precursor to kesterite

Promote Cu_6Sn_5 and Cu_5Zn_8 alloying and crystallization

→ thermal annealing at 350°C in N_2 atmosphere

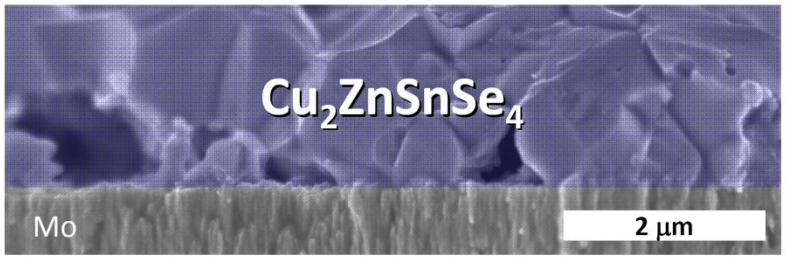


SEM cross-section of alloyed Cu/Sn/Zn stack



Arasimowicz et al., *MRS Proceedings*, 1538, pp 123-129.

t_{anneal} = 4 min.
T = 550°C,
500 mbar,
SnSe, Se



Collaboration with University of Luxembourg (Steichen/Dale)

Further processed to solar cell with efficiency of 5.5%

Conclusions

- "**Liquid metal salts**": low-melting ionic transition metal complexes
- Can be considered as real ionic liquids
- Concept illustrated for different types of ligands and metals
- Metal is part of cation
- Electrolytes with high metal concentration
- Cathodic decomposition of ionic liquid is deposition of metal
- High current densities are possible
- Additives have effect on morphology
- Electrodeposition of smooth layers of copper, silver, zinc, tin
- Cu on Ta electrodeposition for superfilling of electronic vias
- Fast deposition of Cu/Sn/Zn stacks for kesterite solar cells

KU LEUVEN

Thank you!